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⑥ REVERSIBLE INTERMOLECULAR ENERGY TRANSFER BETWEEN CHROMIUM(III)

COMPLEXES IN FLUID SOLUTION,

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Summary

Excitation energy transfer from $Cr(en)_3^{3+}$, $Cr(NH_3)_5(NCS)^{2+}$, trans-$Cr(en)_2(NCS)_2^+$, and cis-$Cr(en)_2(NCS)_2^+$ to $Cr(CN)_6^{3-}$ is observed in room temperature solutions in water, dimethylsulfoxide, or dimethylformamide. The processes were observed by emission intensity measurements and, especially, by lifetime measurements on both the donor and the acceptor emission. The rate of energy transfer is essentially diffusion controlled in all cases and thus not very sensitive to the charge or ligation of the donor. In addition, evidence for reverse excitation energy transfer is presented; the lifetime of $Cr(CN)_6^{3-}$ emission is dependent on the concentration of the Cr(III) ammine. It is shown that in this type of coupled system a full kinetic analysis is required to obtain correct bimolecular energy transfer rate constants as those obtained from conventional Stern-Volmer plots can be seriously in error.

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Chromium(III) complexes display a rich photochemistry under ligand field (LF) irradiation;[1] many exhibit room temperature solution phosphorescence.[2]

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[1] See E. Zinato in "Concepts of Inorganic Photochemistry," A.W. Adamson and P.F. Fleischauer, eds., Wiley, 1975.

[2] (a) D.J. Binet, E.L. Goldberg, and L.S. Forster, J. Phys. Chem., $\underline{72}$, 3017 (1968).

(b) N.A.P. Kane-Maguire and C.H. Langford, Chem. Comm., 895 (1971).

(c) H.F. Wasgestian, J. Phys. Chem., $\underline{76}$, 1947 (1972).

(d) A.W. Adamson, C. Geosling, R. Pribush, and R. Wright, Inorg. Chim. Acta, $\underline{16}$, L5 (1976).

Excitation energy transfer to chromium(III) complexes has also been established in room temperature fluid solutions, first with organic donors,[2a,3] and then

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[3] (a) A.W. Adamson, J.E. Martin, and F. Diomedi-Cammessei, J. Amer. Chem. Soc., $\underline{91}$, 7530 (1969).

(b) V. Balzani, L. Moggi, M.F. Manfrin, F. Bolletta, and G.S. Lawrence, Coord. Chem. Rev., $\underline{15}$, 321 (1975).

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with Ru(bipyridine)$_3^{2+}$.[4] The efficiency of excitation energy transfer for a

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[4] (a) J.N. Demas and A.W. Adamson, J. Amer. Chem. Soc., $\underline{93}$, 1800 (1971).

(b) I. Fujita and H. Kobayashi, Ber. Bunsenges. Phys. Chem., $\underline{76}$, 115 (1972).

(c) F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, J. Amer. Chem. Soc., $\underline{95}$, 7864 (1973).

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given donor, can vary considerably with the nature of the chromium(III) acceptor complex.[3a,5] When the present study was initiated the only case in which both

[5] (a) A. Adamczyk and F. Wilkinson, J. Chem. Soc. Far. II, 68, 2031 (1972).

(b) J.N. Demas and J.W. Addington, J. Amer. Chem. Soc., 96, 3663 (1974).

(c) H.F. Wasgestian and G.S. Hammond, Theor. Chim. Acta, 20, 186 (1971).

donor and acceptor species were chromium(III) complexes was that reported for trans-$Cr(NH_3)_2(NCS)_4^-$ (donor) and $Cr(CN)_6^{3-}$ (acceptor), at $-65°C$.[6] The present

[6] S. Chen and G.B. Porter, J. Amer. Chem. Soc., 92, 3196 (1970).

investigation was undertaken to see if excitation energy transfer could occur between chromium(III) complexes in room temperature solution. We confirm and add to a recent report that such transfer can indeed occur.[7]

[7] F. Bolletta, M. Maestri, and V. Balzani, J. Phys. Chem., 80, 2499 (1976).

The general process is that of Eq. 1. Species B is always $Cr(CN)_6^{3-}$ in this work,

$$^*A + B \underset{k'_q}{\overset{k_q}{\rightleftharpoons}} A + \,^*B \qquad (1)$$
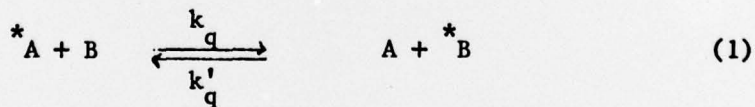
and species A is one of the ammines of Table I. These complexes, especially B, are relatively weak and short-lived emitters in water solution and most measurements were therefore made in dimethylformamide (DMF) or dimethylsulfoxide (DMSO). Conditions were propitious for observing excitation energy transfer from a complex A to $Cr(CN)_6^{3-}$. The latter does not absorb in the wavelength region of the first LF band of any of the A species so that excitation could be restricted to A.[1] On the other hand, the emitting doublet states of the A complexes lie well above that of B in energy so that the forward process (1) should be favored.

Figure 1 shows one sequence of emission spectra for 546 nm excitation of $Cr(NH_3)_5(NCS)^{2+}$ in DMF having various concentrations of B. The shorter wavelength emission is from the ammine, and decreases in intensity with increasing $Cr(CN)_6^{3-}$ concentration; at the same time, the longer wavelength emission from the cyano complex increases in intensity.[8] Clearly excitation energy transfer

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[8] The emission yields were obtained with the use of a modified Aminco-Bowman spectrofluorimeter (Model 4-8203D) (see N.A.P. Kane-Maguire, J.E. Phifer, and C.G. Toney, Inorg. Chem., 15, 593 (1976).

One might suppose, in a sequence such as this, that a crossing point should be invariant. These emission spectra are for a kinetic situation, however, for which the sum of the concentrations of the emitting states, $(^{*}A + ^{*}B)$, is not a constant. No "isosbestic" behavior is expected, nor observed.

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occurs. Analogous results were obtained in DMSO solution. In aqueous solution the intensity of $^{*}A$ emission again decreases with increasing $Cr(CN)_6^{3-}$ concentration. We could not establish, however, whether quenching was accompanied by excitation energy transfer since aqueous $Cr(CN)_6^{3-}$ does not detectably emit. Ion association was minimized throughout by making the solutions 0.5 M in neutral electrolyte, KCl in the case of aqueous systems, and $[(C_4H_9)_4N](ClO_4)$ for the aprotic solvents, and appeared not to be important.[9]

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[9] (a) The spectra of mixtures were essentially identical with those of the summed spectra of separate solutions, in either DMF or DMSO, and from 390 to 600 nm. (b) The Stern-Volmer quenching plot for $Cr(NH_3)_5(NCS)^{2+}$ showed some upward curvature, indicative of ion association;[3b,5b,10] the plot was linear, however, with the 0.5 M neutral electrolyte present. (c) With neutral electrolyte, the slopes of the intensity and lifetime Stern-Volmer quenching plots were essentially

the same. Thus for aqueous $Cr(en)_3^{3+}$ at $22^{\circ}C$ the respective values were 550 and 582 M^{-1}.

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[10] F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, J. Phys. Chem., $\underline{78}$, 1374 (1974).

Measurements of lifetimes,[11] τ, revealed an important complexity. Not

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[11] These were obtained by pulse excitation using 530 nm, 20 nsec pulses from the Q-switched, frequency doubled Nd laser system of Ref. 2d. Solutions were changed frequently to avoid accumulation of photoproducts (from the ammine).

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only did τ_{*A} decrease with increasing B concentration, but also τ_{*B} <u>decreased with increasing A concentration</u>. Reverse excitation energy transfer (Eq. 1) evidently occurred. Plots of $1/\tau_{*A}$ vs. [B] were linear, as were those of $1/\tau_{*B}$ vs. [A], the slopes giving the Stern-Volmer rate constants $k_{q,app.}$ and $k'_{q,app.}$. Stern-Volmer kinetics are inadequate for our coupled reaction scheme, however. The scheme is:

$$(A,P) \xleftarrow{\quad k_{21} \quad} {}^*A \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} {}^*B \xrightarrow{\quad k_{34} \quad} (B,P') \qquad (2)$$
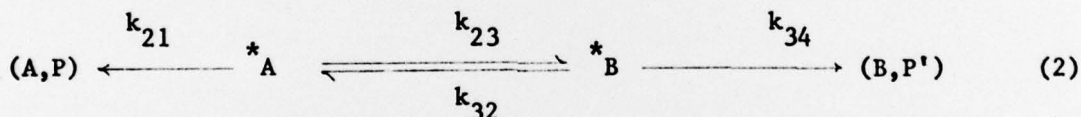
where k_{23} and k_{32} are the pseudo first order rate constants $k_q[B]$ and $k'_q[A]$, respectively, k_{21} is the sum of all rate constants for the exiting of ${}^*A$ from the system (to A or to photoproducts P), and k_{34} is the sum for the exiting of ${}^*B$ (to B or to photoproducts P'). The general solution for coupled first order rate processes is well known;[12] that for equation (2) is:

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[12] See S.W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, 1960, p. 39.

$$^*A = \frac{^*A_o}{\lambda_2-\lambda_1} \quad [(\lambda_2-\alpha)e^{-\lambda_1 t} - (\lambda_1-\alpha)e^{-\lambda_2 t}] + \frac{^*B_o \, k_{32}}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t})$$

(3)

$$^*B = \frac{^*A_o \, k_{23}}{\lambda_2-\lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + \frac{^*B_o}{\lambda_2-\lambda_1}[(\lambda_2-\beta)e^{-\lambda_1 t} - (\lambda_1-\beta)e^{-\lambda_2 t}]$$

where

$$2\lambda_{1,2} = (\alpha+\beta) \pm [(\alpha-\beta)^2 + 4k_{23}\, k_{32}]^{\frac{1}{2}}$$

(4)

and $\alpha = k_{21} + k_{23}$ and $\beta = k_{34} + k_{32}$. In our case, $^*B_o = 0$. Four quantities are known from each set of lifetime measurements: k_{21} and k_{34} from the lifetimes of $^*A$ and $^*B$ in the absence of bimolecular quenching, and λ_1 and λ_2, the decay times with both A and B present; k_{23} and k_{32} may then be found from equation (4), and hence k_q and k'_q. A set of observed and calculated decay plots is shown in Figure 2.

Because of the coupling of rate processes, k_q and k'_q are not the same as the apparent values from the Stern-Volmer slopes. For our systems, expansions correct in first order give

$$k_{q,app.}/k_q = 1 + k_{32}/k_{23}; \quad k'_{q,app.}/k'_q = (k_{21} - k_{32})/k_{23}$$

(5)

The correction is less than 10% in the case of $k_{q,app.}$, but $k'_{q,app.}/k'_q$ may be 0.1 or lower--see Table I. Thus where back excitation energy transfer occurs, Stern-Volmer rate constants can be highly in error.

Turning to the results, the k_q values in Table I are at about the expectation for rate limiting diffusional encounters; they also display the expected inverse dependence on solvent viscosity ($\eta_{DMSO}/\eta_{DMF} = 2.5$ at $25^{\circ}C$), as do the k'_q values.

The $k_{q,app.}$ values for the four ammine donors in DMF show little variation with charge or ligation. By contrast, with $Ru(bipyridine)_3^{2+}$ as donor, $k_{q,app.}$ varied by ten fold over a series of $Cr(en)_2XY^+$ acceptors[4c] and by a thousand fold if the series includes $Cr(CN)_6^{3-}$. The excited state of $Ru(bipyridine)_3^{2+}$ is charge transfer in character and likely is highly polarizable; this could explain the sensitivity of the quenching rate to the detailed nature of the acceptor. The behavior we observed may be the more normal one for excitation energy transfer between LF excited states.

Temperature studies are in progress to obtain an important quantity, the activation energy difference between k_q and k'_q. This difference gives a kinetic value for the energy difference between the doublet excited states of the Cr(III) complexes. Preliminary results place this value at about 10 kcal/mole for A = $\underline{trans}-Cr(en)_2(NCS)_2^+$, or at about the spectroscopic value.

Table I. Emission and Excitation Energy Transfer Rate Constants at $25^{\circ}C$[a]

Complex (Solvent)	Emission Lifetime[b] τ°, (μsec)	Bimolecular Rate Constants, $M^{-1} \mu sec^{-1}$			
		From Eq. (4)		From Stern-Volmer Plots	
		k_q	k'_q	$k_{q,app.}$	$k'_{q,app.}$
$Cr(en)_3^{3+}$ (H_2O)	1.3,[c]1.0				
(DMF)	0.95			613	
$Cr(NH_3)_5(NCS)^{2+}$ (DMF)	0.27, 1.1[d]			894	
trans-$Cr(en)_2(NCS)_2^+$					
(H_2O)	2.05				
(DMF)	4.14	654	4.46	722	0.269
(DMSO)	3.16	282	2.52	270	0.274
cis-$Cr(en)_2(NCS)_2^+$					
(DMF)	0.24			660	
$Cr(CN)_6^{3-}$(H_2O)	–				
(DMF)	540[e], 491				
(DMSO)	116				

(a) Data from this work unless otherwise indicated. Solutions were 0.01-0.04 M in A and 0.001-0.004 M in B. (b) For the ammines $\tau^{\circ} = 1/k_{21}$ and for $Cr(CN)_6^{3-}$, $\tau^{\circ} = 1/k_{34}$. (c) H.F. Wasgestian, R. Ballardine, G. Varani, L. Moggi, and V. Balzani, J. Phys. Chem., 77, 2614 (1973) and Ref. 2c. (d) $3^{\circ}C$. (e) See Ref. 2c.

Legends.

Figure 1. Steady-state emission spectra on 546 nm excitation of 0.012 M $Cr(NH_3)_5(NCS)^{2+}$ in DMF containing the following concentrations of $Cr(CN)_6^{3-}$: (i) none, (2) 0.0038 M, (3) 0.0057 M, (4) 0.0114 M.

Figure 2. Transient emission following 530 nm pulse excitation of a DMF solution 0.0105 M in trans-$Cr(en)_2(NCS)_2^+$ and 0.00306 M in $Cr(CN)_6^{3-}$. Curve 1: emission from trans-$Cr(en)_2(NCS)_2^+$ measured at 728 nm. Curve 2: emission from $Cr(CN)_6^{3-}$, measured at 810 nm. Solid lines: calculated curves; points: observed behavior as read from oscilloscope photographs.